POTATO STARCH FACTORY WASTE EFFLUENTS I. RECOVERY OF POTASSIUM AND OTHER INORGANIC CATIONS[1,2]

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ABSTRACT

A process for recovery of valuable constituents from potato starch factory waste water is under development. Recovery of protein, amino acids, organic acids and a potash fertilizer should reduce the BOD markedly and provide a more economic waste treatment. Fertilizers containing 32-42% K_2SO_4, 53-56% $(NH_4)_2SO_4$, and 1% amino acids as well as trace elements from the tuber can be made as a byproduct of the amino acid recovery process. Data needed for design of the potash recovery part of the process are given, including: C/C_0 curves, exhaustion and regeneration rates, resin capacities and product recoveries, and a flow sheet for a proposed process.

RESUMEN

Existe un proceso en desarrollo para la recuperación de valiosos constituyentes del agua de desperdicio de las fábricas de almidón de papa. La recuperación de proteína, amino ácidos, ácidos orgánicos y un fertilizante de potasa reducirán grandemente el BOD y proporcionarán un tratamiento de desperdicio más económico. Los fertilizantes que contengan 32-42% K_2SO_4, 53-56% $(NH_4)_2SO_4$, y 1% de amino ácidos, así como elementos indicadores del tubérculo pueden ser convertidos en un biproducto del proceso de recuperación del amino ácido. Los datos necesarios para el diseño de la parte de recuperación del proceso incluyen: curvas de C/C_0, clasificaciones de agotamiento y regeneración, capacidades de resina y recuperación de producto, y una hoja de flow para el procedimiento propuesto.

The problem of stream pollution by waste effluents from food processing plants has become one of major importance in the United States. The potato starch processing industry contributes considerably to this problem.

The secondary (soluble) wastes are present in relatively low concentrations in the large volume effluents from potato starch factories. They are composed roughly as follows: protein 15%; amino compound 30%; organic acids 30%; sugars 15%; and potassium 10%. The biochemical oxygen demand of this mixture is extremely high and, therefore, requires

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[4]Mention of brand or firm names does not constitute an endorsement by the Department of Agricultuure over others of a similar nature not mentioneq.
[5]K as K_2O.

an efficient type of sewage or waste treatment. The potato starch industry itself is a disposal operation operating on a slim margin. It cannot absorb added waste treatment costs because of heavy market competition from other starches. The process described would reduce the amount of waste, and the return for materials recovered may cover the cost of the process. A commercial process for protein recovery is in use in Europe (4). A process for recovering amino acids from potato starch factory wastes was reported from this Laboratory (1, 2), and industrial interest has been shown in the product. No information on the economic feasibility was obtained. Since this report, modifications of ion exchange processes have been developed which wil improve the efficiency of the over-all process.

Because of the urgent need a project was initiated at this Laboratory to provide a complete treatment of potato starch factory secondary waste. The proposed process would consist of five steps: (i) concentration of dilute waste to approximately 4-5% solids by reverse osmosis or as much as possible improved water use; (ii) precipitation and recovery of protein by steam injection or other suitable method; (iii) separation and recovery of a fertilizer mixture of potassium and other inorganic cations by ion exchange; (iv) separation and recovery of amino compounds by ion exchange; and (v) recovery of organic acids (mainly citric) and phosphates by ion exchange.

Materials and Methods

All ion-exchange studies were performed using 1-inch diameter, 24-inch long, water-jacketed, glass columns containing 300 ml of wet IR 120 (H^+) resin, 16 to 50 mesh, (Rohm and Haas,[4] Philadelphia, Pa.) Exhaustion and elution was monitored by pH measurements on the flowing stream, and potassium ion concentrations by flame photometry and electrical conductivity. Constant flow pumps were employed for all streams; waste, wash water, and eluting agents. Analysis for trace elements were made by atomic absorption methods.

Two types of waste were used in the experimental work. One type, "minimum dilution waste," is simply a deproteinized extract of raw potatoes having a total dissolved solids (TDS) content of approximately 3.6%. The other type, "reverse osmosis concentrate," was made by diluting the minimum dilution waste (before deproteinization) to ca. 0.5%, then concentrating to app. 2.0% by reverse osmosis. After deproteinization this concentrate is about 1.4% TDS.

Results and Discussion

Separation and recovery of potassium

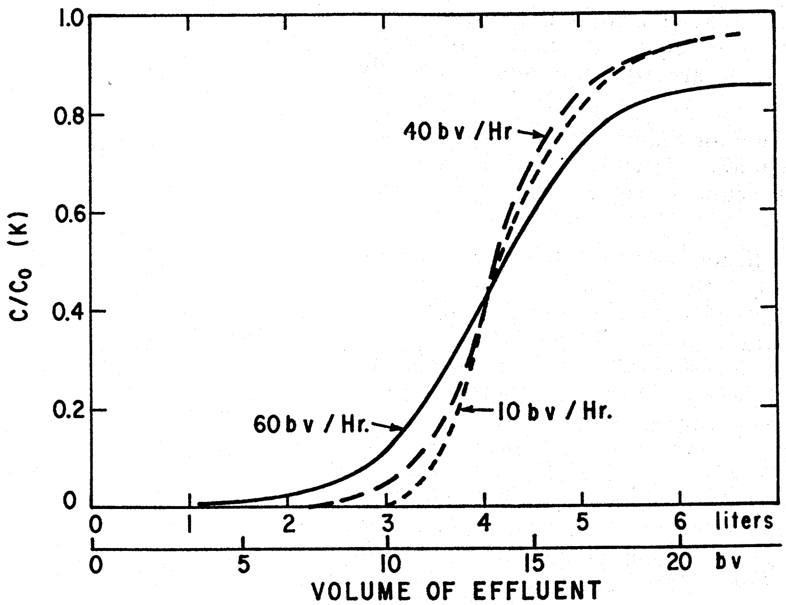
When deproteinized potato waste water is passed through a cation exchange column both the amino compounds and the potassium and other inorganic cations are adsorbed, but the potassium and other inorganic cations can displace the amino compounds already adsorbed, which are then readsorbed at sites lower on the column. If enough waste is treated, all the amino compounds are eventually displaced and appear in the effluent.

Since potassium is a major constituent of the waste water (about 12% of the TDS of the protein-free waste), a potassium recovery step was incorporated into the ion exchange process. This is advantageous for two reasons. First, elution of the potassium from the column with sulfuric acid and subsequent neutralization yields a useful fertilizer mixture, and secondly, the amino compounds are adsorbed more efficiently from a potassium-free waste water.

Optimum conditions were determined for the adsorption of potasssium on the column and its subsequent elution. Variables studied were exhaustion and elution flow rates, potassium concentration of the waste water used as feed, and temperature of feed.

Exhaustion step — Concentration history curves (at 30 C) were obtained at various flow rates (3), and are presented in Figs. 1 and 2. A concentration history curve is a plot of the ratio of the concentration of the effluent to the concentration of the influent (C/C_0), both with respect to potassium, against the put-through in volume of effluent or weight of constituent. This curve shows the fraction of the constituent being exchanged by the resin at any stage during the exhaustion step. In the beginning, when the C/C_0 value is near zero, practically all the potassium is being adsorbed, the leakage is near zero, and the effluent is essentially potassium-free. At the top of the curve when the C/C_0 value approaches 1 the column is saturated, and the leakage is approaching 100%. The curves in Fig. 1 were obtained with minimum dilution waste water that contained approximately 3.6% TDS and 0.55% potassium. The three flow rates studied were 10, 40, and 60 bed volumes per hour (bv/hr). The curves show the column effectively exchanged potassium and very little efficiency was lost when the flow rate was increased from 10 to 40 bv/hr. The curves are relatively steep, indicating good exchange conditions. At 60 bv/hr the curves flattened out, somewhat. The curves of Fig. 2 were obtained using the reverse osmosis concentrate, which contained 1.4% TDS and 0.16% potassium. The flow rates used were 40, 60, and 105 bv/hr. Essentially the same types of curves were obtained as in Fig. 1.

An important variable considered was the effect of the concentration of the waste water used on the exchange rate. To carry out this study an attempt was made to compare the 3.6% TDS minimum dilution waste and the 1.4% TDS reverse osmosis concentrate. These two feeds on an approximate equal weight of potassium put-thru per unit time basis are compared in Fig. 3. In this case the C/C_0 value was plotted against the weight of potassium put thru the column. An unexpected result was observed. The capacity of the column for potassium was reduced when using the reverse osmosis concentrate. This difference is explained by the fact that the reverse osmosis concentrate was obtained by diluting the 4% extract with 7 volumes of tap water. Tap water, in this area (northwestern suburbs of Philadelphia) contains approximately 75 ppm of calcium and magensium combined, calcium being predominant. The 12 liters of reverse osmosis concentrate used to saturate the column thus contained ca. 3.0 g of calcium and magnesium (as calcium) due to the tap water. This amount of calcium would reduce the potassium capacity by ca. 5.8 g, which is in the range of the reduction observed. This illustrates the imporatnce of the water quality available at the process site.



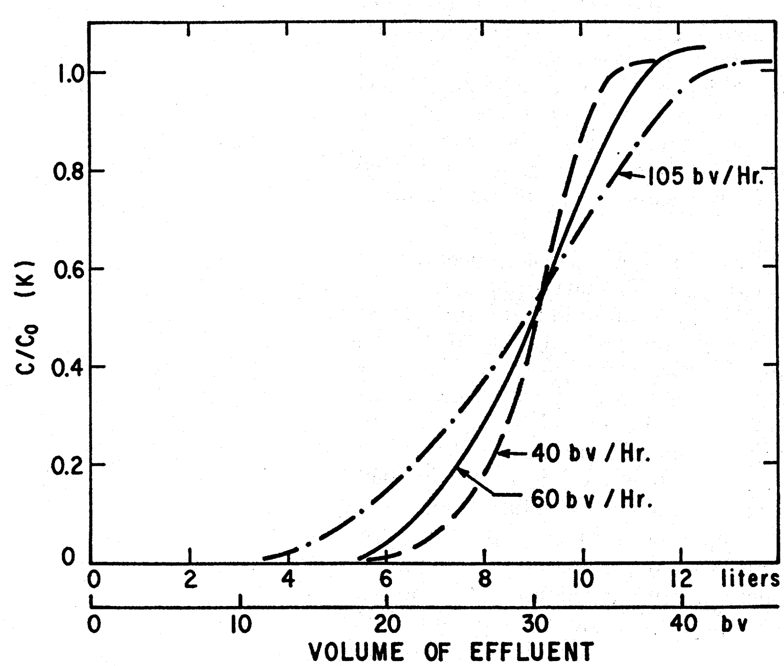
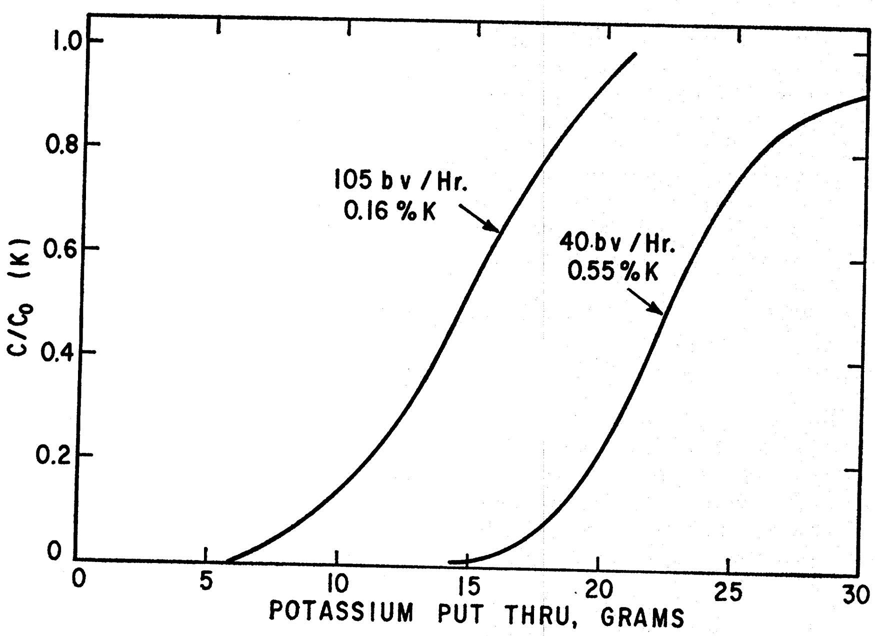


FIG. 1.—Effect of flow rate on column efficiency. Use of minimum dilution waste 3.6% TDS, 0.55% K. (Top)

FIG. 2.—Effect of flow rate on column efficiency. Use of reverse osmosis concentrate feed, 1.4% TDS, 0.16% K.



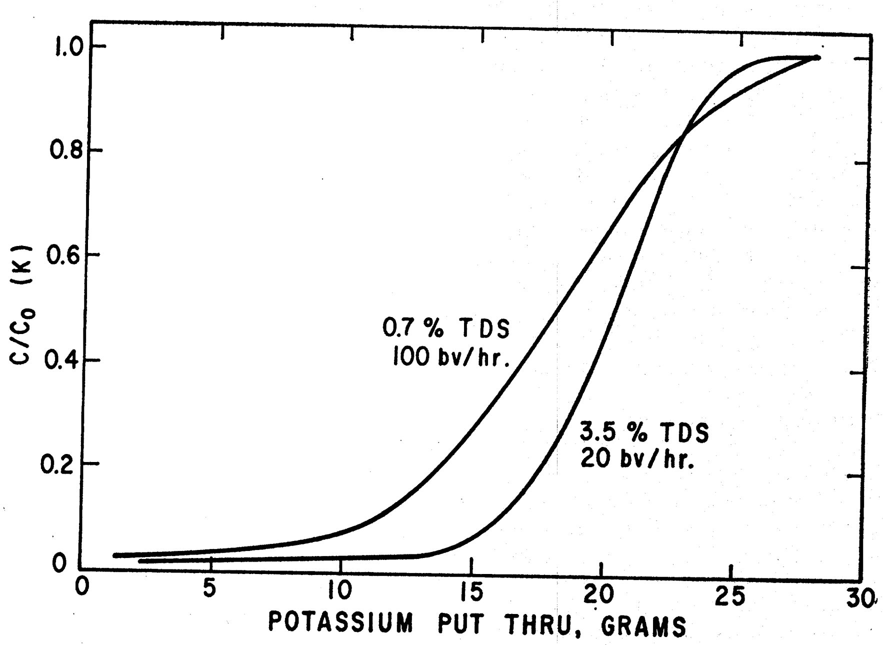


FIG. 3.—Effect of type of feed on column efficiency. (Top)
FIG. 4.—Effect of concentration of feed on column efficiency.

To make a better comparison of the effect of feed concentration, a 10 liter batch of the 3.6% TDS feed was divided into two equal portions. One was run thru the column directly at a flow rate of 20 bv/hr and the other was diulted to 0.7% TDS with distilled water and run thru the column at a flow rate of 100 bv/hr. Thus, the weight of potassium put through per unit time was equal. From the plot of the concentration history curves obtained, Fig. 4, it was obvious that a more efficient exchange rate was obtained with the higher concentration. This coupled with the operational advantages of handling smaller volumes, made it advantageous, but not essential, to use a more concentrated feed.

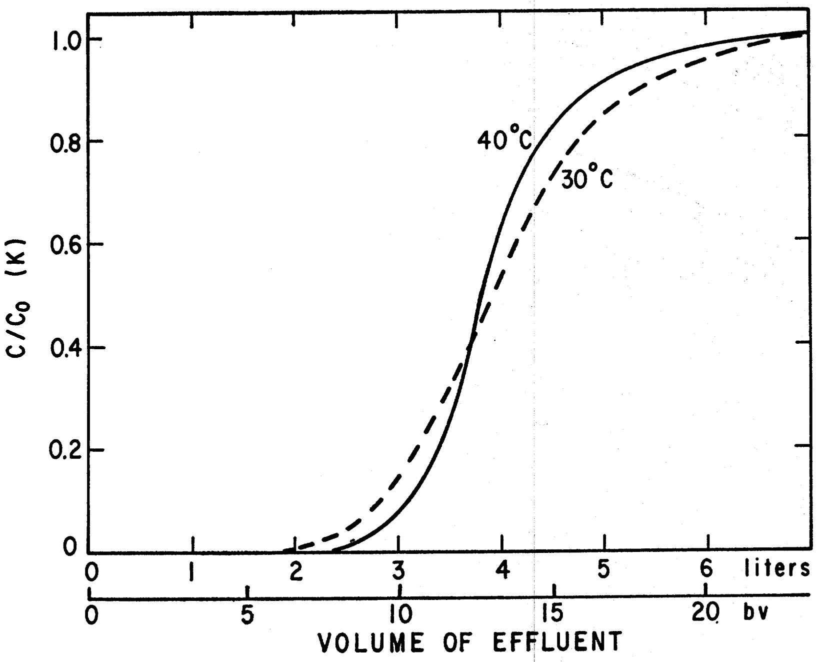
The effect of temperature on the exchange rate was studied. Concentration history curves were obtained at 30 C and 40 C using the minimum dilution waste at 40 bv/hr. Fig. 5 shows that an increase in temperature does increase the exchange rate.

Measurement of conductance of the effluent was found to be a convenient and effective means of monitoring the adsorption of potassium. Fig. 6 compares a concentration history curve obtained by flame photometric determination of potassium and a curve obtained by measurement of conductance. A minimum is obtained in the conductance curve which coincides with the start of the break-through of potassium as measured by flame photometry.

Elution (or regeneration) step — The elution of potassium from the column is carried out with H_2SO_4. This also regenerates the column and readies it for the next exhaustion cycle. Fig. 7 compares the regeneration efficiency of 5 and 10% concentrations of H_2SO_4. Concentration history curves (based on equivalents of acid in the eluant and eluate) are plotted. From the shape of the curves it is obvious that the 10% H_2SO_4 was considerably more efficient than the 5%. Fig. 8 presents regeneration data using 10% H_2SO_4 at 7 and 15 bv/hr flow rate. The curves are very similar; thus it can be concluded that regeneration flow rate is not a critical factor. From the standpoint of the elution of potassium the same conclusion was drawn, based on a series of experiments in which the flow rate was varied from 5 to 20 bv/hr. The maximum potassium concentration obtained was plotted against flow rate for the series. In these experiments the column was loaded to the 20% leakage level. A statistical analysis of the data showed that the rate of poassium elution was independent of flow rate.

Typical elution curves from a saturated column (100% leakage) and a column loaded to approximately 20% leakage are shown in Fig. 9. The minimum dilution waste was used to exhaust the column in both cases. Elution flow rate was 10 bv/hr. A total of 17.1 g of potassium was eluted from the saturated column in the middle fraction and 15.5 g from the unsaturated column. This represents about a 10% gain in yield from the saturated column.

The acid eluate from the potassium column is divided into three parts — void, middle, and tailing fractions. Fig. 9 shows the volume, in bv, of these fractions. The void fraction can be recycled as wash water before regeneration. The middle fraction containing the potassium is neutralized with conc. NH_4OH. When dried, a fertilizer having an NPK[5] analysis of 12-0-17 or 11-0-22 was obtained, depending on the type of



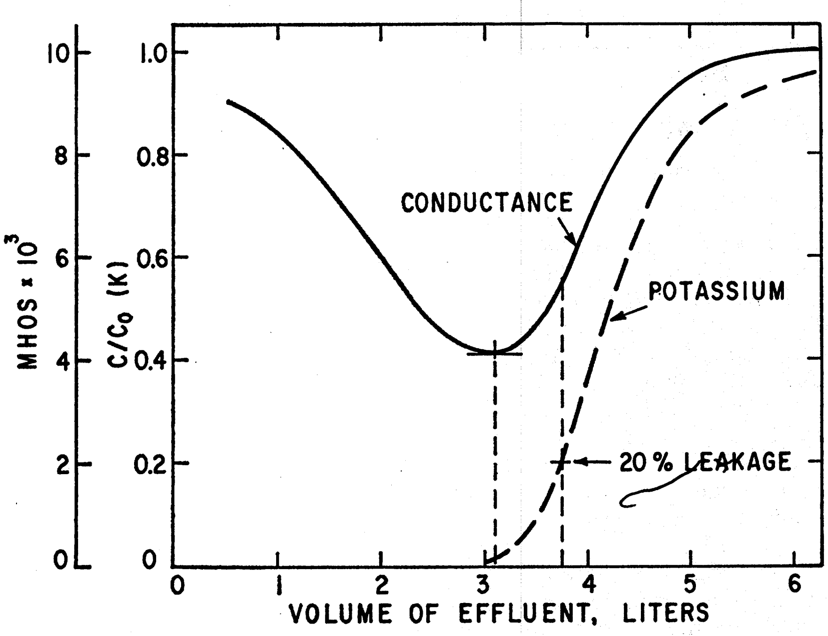


FIG. 5.—Effect of temperature of feed on column efficiency (flow rate 40 bv/hr). (Top)
FIG. 6.—Comparison of concentration history curves obtained from potassium data by analysis and by measurement of conductance.

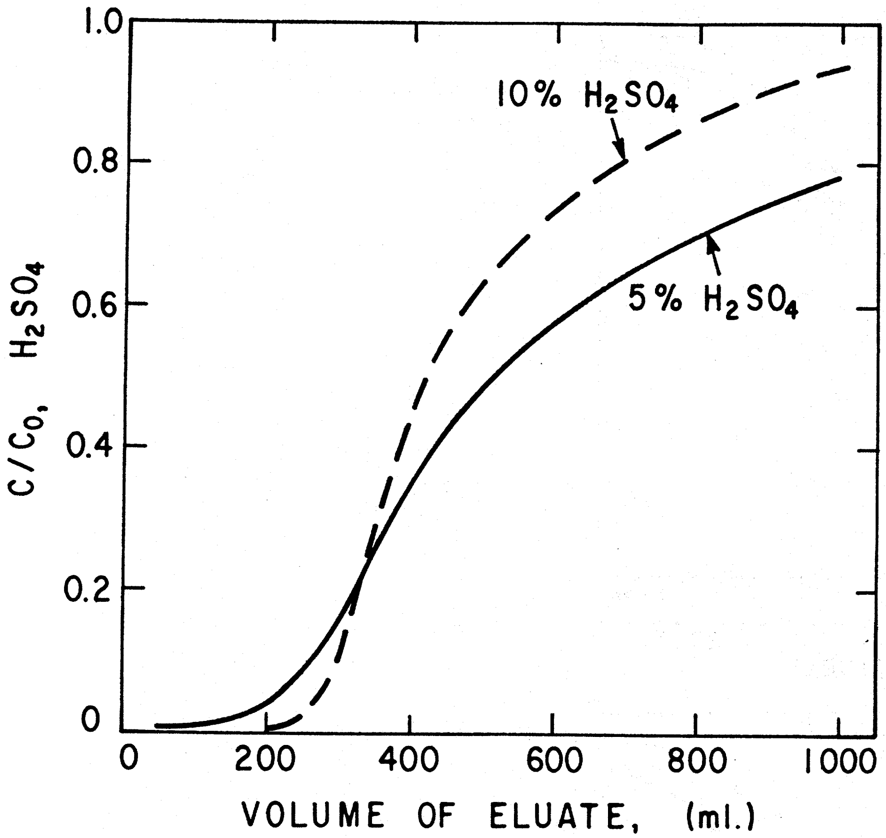


FIG. 7.—Effect of concentration of sulfuric acid on efficiency of regeneration (flow rate = 2 bv/hr).

feed used to exhaust the column. The lower K analysis is obtained using the reverse osmosis conc. The tailing fraction is still highly acidic, approximately 1.5 N; and is reused as the initial eluant (or regenerant) in the next cycle. This then becomes the middle fraction of the next eluate. As depicted in Fig. 9, this initial eluant is followed by 2 bv of fresh 10% H_2SO_4 and 1 bv of water which becomes the tailing fraction of the next eluate and thus is reused in the succeeding cycle, etc.

The above description calls for 2.5 bv of recycled H_2SO_4 and 2 bv of fresh 10% H_2SO_4 to elute and regenerate the column. This is a very high level of regeneration. It is equivalent to approximately 25 lbs of 66° Bé H_2SO_4/cu ft. At this level the column should be operating very close to its theoretical capacity.

From the above experimental data, a schematic drawing representing a proposed three column process was constructed. This is presented in Fig. 10. In any one cycle one column is being loaded, the next is acting as scavenger to trap potassium leaking from the loading column, and the third is being eluted. Using a scavenger permits the columns to be loaded

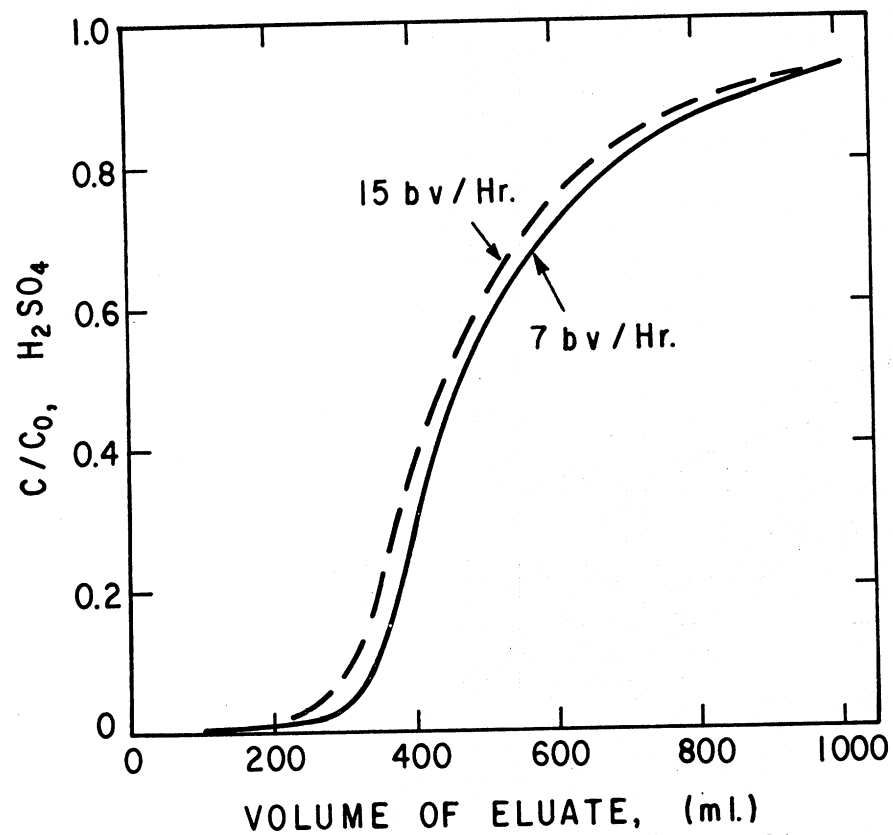


FIG. 8.—Effect of flow rate on efficiency of regeneration (10% H_2SO_4).

to saturation. An upflow technique is used for the exhaustion step. This eliminates the need to backwash between cycles.

A specific example, based on a potato starch plant producing 30 tons of starch per 16 hr day can be oultined as follows: assume a waste effluent from such a plant to be 6,750 gal/hr containing 2.4% TDS. Protein precipitation and removal would lower the TDS to approximately 2.0%. Based on a flow rate of 30 bv/hr, this would require three columns of approximately 225 gal (30.0 cu ft.) each, of cation exchange resin. Assuming a potassium content of 12% of the TDS, after protein removal, this process would yield approximately 1.1 tons of potassium/day. Translating this value to the fertilizer product (ammonia neutralization) yields a weight of 5.8 tons of solids/day. As produced, it is about 11% solids.

Other inorganic cations originally present in the potato, and those introduced by the water used in processing are adsorbed and eluted along with the potassium. Table 1 gives a complete analysis of the fertilizer products. Less potassium and more calcium, magnesium and sodium were obtained when a reverse osmosis concentrate was used to exhaust the column. This was due to the presence of the latter elements in the tap water employed to dilute the 3.6% TDS waste.

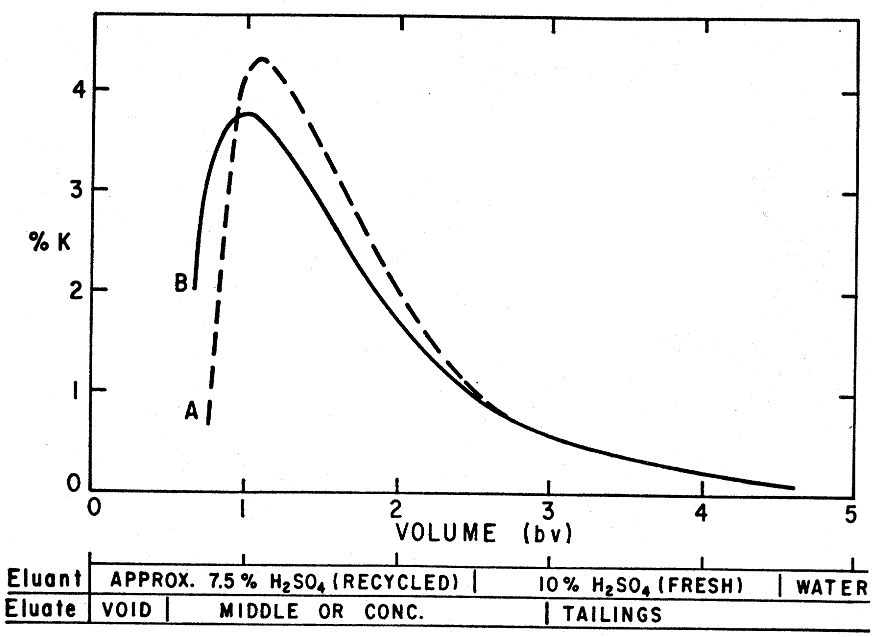
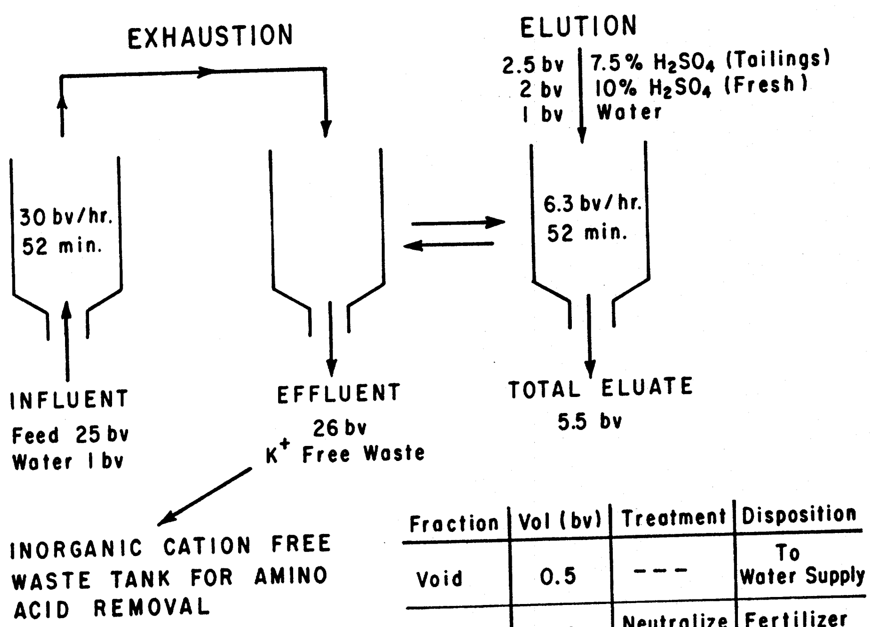


FIG. 9.—Effect of degree of loading on elution efficiency. Feed = 3.6% TDS (40 bv/hr). A = Loaded to saturation (100% leakage). B = Loaded to approximately 20% leakage. Elution flow rate = 10 bv/hr.

TABLE 1.—Composition of fertilizer products produced from starch factory waste water.

	Waste water used to exhaust column			
	Minimum dilution waste		Reverse osmosis conc.	
	% Dry basis	ppm Dry basis as element	% Dry basis	ppm Dry basis as element
$(NH_4)_2SO_4$	53.2	....	56.1	....
K_2SO_4	41.4	....	31.9	....
$CaSO_4$	1.7	5000	5.2	15000
$MgSO_4$	1.7	3400	4.1	8300
Na_2SO_4	1.2	3800	2.0	6000
$Fe_2(SO_4)_3$	......	30	......	30
$ZnSO_4$	......	18	......	18
$CuSO_2$	......	8	......	8
$CrSO_4$	......	4	......	4
Amino cmpds.	0.8		0.7	
	100.0		100.0	



Fraction	Vol (bv)	Treatment	Disposition
Void	0.5	---	To Water Supply
Middle	2.5	Neutralize With NH_3	Fertilizer Product
Tailing	2.5	---	Eluent for Next Cycle

FIG. 10.—Suggested potassium recovery process by use of cation exchange.

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